

Title	Reactivity of Acetylene in Vinylether Synthesis
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$$M=(22.9\pm 3.02)\times 10^{10} \text{ [1/(moles/ml.)min.]}$$

2. Maximum Point of the Reaction Rate.

The optimum relative titer of iodine with respect to bromine was expressed as follows :

$$Y=[\{4\alpha\beta/(K_1\tau^2)\}\{m^2/(m+1)\}+\{(m/m+1)\}]X \quad (4)$$

where X and Y are the titers of bromine and iodine, and K_1, α, β and τ are constants. With toluene as reactant, since m is equal to 3, equation (4) is transformed to equation (5) in just the same way as with benzene.

$$Y=[\{4\alpha\beta/(K_1\tau^2)\}(9/4)+(3/4)]X \quad (5)$$

Equation (5) suggests the optimum ratio of iodine to bromine is approximately equal to 3/4, because the first term is negligibly small compared with the second. This relation was ascertained experimentally.

3. Induction Period

An induction period was found in the bromination. Examinations have revealed that the induction period becomes longer, (a) the lower the concentrations of halogens, (b) the less polar the solvent, and (c) the less reactive the hydrocarbon. Thus the induction period is not appreciable for the brominations with halogen in higher concentration (Bruner), or with reactive mesitylene as reactant (Robertson), or with toluene in chloroform (the present authors). Furthermore, the induction period was not affected by the addition of benzoyl peroxide or molecular oxygen.

From the above examinations, it was reasonably assumed that this induction period is not resulted from a radical reaction, but from an ionic one. It seems the reaction proceeds through an intermediate formation, in which iodine bromide must participate. Since equation (1) can fit only the data from the reaction which has attained to a stationary state, the overall rate of the reaction will be smaller than that expected from equation (1) before the concentration of the intermediate attains to the equilibrium concentration. Thus the longer time will be required for the reactions under the conditions (a), (b) and (c). This time can presumably be interpreted as the induction period.

14. Reactivity of Acetylene in Vinylether Synthesis

Junji FURUKAWA, Tatsuo ANDO and Mitsuru YOKOYAMA

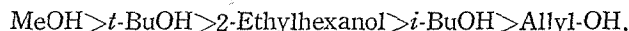
(Oda Laboratory)

It is well-known that the rate of vinylation of alcohol is markedly affected by the structure of alcohol used, but there have not yet been available any quantitative

studies about the vinylation: most of the published papers dealing with this problem are only qualitative ones, and not a few discrepancies are found among them. Reaction mechanism proposed by W.E.Hanford *et al.* also has some weak points.

The authors have examined the relationship between the rate of vinylation and the acidity of alcohol and obtained the following results.

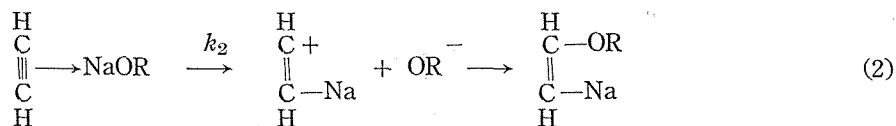
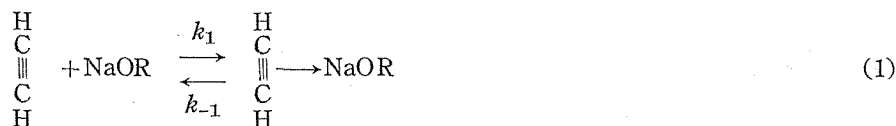
Firstly, the rate of vinylation decreases in the order :



The rate becomes smaller, the larger the acidity of alcohol with the exception of methanol.

Secondly, the vinylation of isobutanol is retarded by the addition of methanol, allyl alcohol or phenol which is more acidic than the former. Furthermore equimolecular quantity of phenol to the catalyst, *i.e.* sodium, does completely suppress the vinylation of isobutanol.

From these results, the following mechanism can be assumed.



The equilibrium (1), π -complex formation, is attained rapidly, whereas equation (2), dissociation of OR^- , proceeds only slowly. Therefore the overall rate (v) of the reaction is determined by equation (2) as follows.

$$v = k_2[\pi][\text{OR}^-] \quad (4)$$

At the stationary state of the reaction, the following relation should exist;

$$d[\pi]/dt = k_1[\text{HC}\equiv\text{CH}][\text{NaOR}] - k_{-1}[\pi] - k_2[\pi][\text{OR}^-] = 0 \quad (5)$$

And hence,

$$[\pi] = k_1[\text{HC}\equiv\text{CH}][\text{NaOR}] / \{k_{-1} + k_2[\text{OR}^-]\}.$$

If k_{-1} is much larger than k_2 , it follows that

$$v = k_1 k_2 [\text{HC}\equiv\text{CH}][\text{NaOR}][\text{OR}^-] / k_{-1} \text{ or } v = K k_2 [\text{HC}\equiv\text{CH}][\text{NaOR}][\text{OR}^-] \quad (6)$$

where K is equal to k_1/k_{-1} .

From equation (6), it is reasonably expected that the acidity of alcohol is one of the most important factors that affect the rate of vinylation.

As is shown in our results, since the lower acidic alcohol is faster vinylated, it can be assumed that the undissociated alcohol does participate in the actual vinylation.

If the sodium atom in an alcoholate, NaOR, is highly ionized, the π -complex cannot be formed, because the sodium is most stable in its ionic form, Na⁺.

Thus phenol deprives the isobutylate of the sodium atom; but the sodium in phenolate is so highly ionized that the reaction (1) cannot occur, vinylation being markedly retarded.

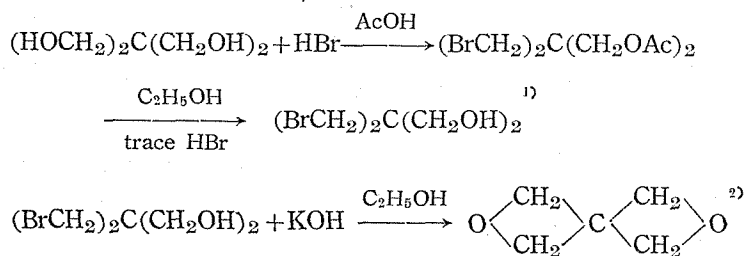
It will be well understood from the similar consideration that the vinylations of the more acidic compounds, *e.g.* acetic acid or phenol can be performed effectively through their undissociated salts such as Hg, Cd, or Zn salt instead of alkali salts.

15. The Synthesis and Chemical Behaviours of Dioxaspiroheptane

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Synthesis of Dioxaspiroheptane (D.A.H.).



1) Beyaert, Hansens: *Natuurw. Tijdschr.* **22**, 249-69(1940); *C.A.*, **37**, 5373(1943).

2) Backer, Schurink: *Rec. trav. chim.*, **53**, 812 (1934).

According to the above schema, the authors have synthesized dioxaspiroheptane in 20% yield. D.A.H. (m.p. 89°C) is sublimable in crystal with slight camphor-like odour, easily soluble in water and alcohol, and slightly soluble in ether.

Polymerisation. When 0.5184 g. of D.A.H. was heated at 150°C for 6 hrs. with 0.0725 g. of caustic potash in sealed tube, reddish brown clear resinous product was obtained. This resin is hard and brittle. This resinous product was crushed and washed by hot water. It is insoluble in ordinary solvents and chars slowly at about 300°C without showing melting point.